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# NMR Studies of Molecular Hydrogen in Hydrogenated Amorphous Silicon

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## ABSTRACT

Using $^1$H nuclear magnetic resonance (NMR), the concentrations of molecular hydrogen have been measured directly in hydrogenated amorphous silicon made by the hot wire chemical vapor deposition (HWCVD) technique. The NMR experiments employed a Jeener-Broekhaert three-pulse sequence. The molecular hydrogen concentrations are about an order of magnitude greater than those inferred from spin-lattice relaxation time measurements. The HWCVD samples have lower transition temperatures for freezing of the molecular hydrogen motion than those prepared by the plasma enhanced CVD method. This behavior is attributed to a more ordered silicon structure in the HWCVD samples.

## 1. Introduction

Hydrogen plays a crucial role in determining the structural and electronic properties of hydrogenated amorphous silicon (a-Si:H). In typical samples prepared by plasma enhanced chemical vapor deposition (PECVD), the hydrogen concentration is about 10 to 15 at. %. Most of the hydrogen atoms are bonded to silicon atoms. About 30 % of these bonded hydrogen atoms are isolated from one another (dilute); the rest of the bonded hydrogen atoms are clustered. These two different hydrogen environments can be distinguished by proton nuclear magnetic resonance ($^1$H NMR). In $^1$H NMR the dilute hydrogen produces a narrow line (~ 4 kHz) that is best fitted by a Lorentzian function, while the clustered hydrogen produces a broader line (~ 25 kHz) that is best fitted by a Gaussian function [1,2].

The presence of a small amount of non-bonded molecular hydrogen in a-Si:H was first proposed by Conradi and Norberg to explain the temperature dependence of the spin-lattice-relaxation time ($T_1$) of bonded hydrogen [3]. From measurements of $T_1$ of bonded H, the concentration of $H_2$ is about 1 % of the total hydrogen in standard samples of a-Si:H made by the PECVD technique [2]. However, this model is based on the assumption that all ortho-$H_2$ molecules contribute to spin-lattice-relaxation of the bonded hydrogen atoms. Later experimental evidence has shown that this assumption is not correct [4].

It has been recently suggested that molecular hydrogen may play an important role in the metastable effects that are ubiquitous in a-Si:H [5]. Therefore, it is of importance to investigate the presence of hydrogen molecules in a-Si:H in more detail with new NMR techniques.

## 2. Experimental Details

Since the NMR lineshape of ortho-$H_2$ is very broad, the simplest NMR techniques, such as measurements of the free induction decay, are not useful. In order to obtain accurate and direct measurements of the ortho-$H_2$ we employed a Jeener-Broekhaert three-pulse sequence as described elsewhere [6]. By extrapolating the echo amplitudes to zero pulse separation between both the first and second pulses and the second and third pulses, one obtains a direct measure of the concentration of molecular hydrogen in the sample regardless of whether or not the molecules contribute to the spin-lattice relaxation of bonded hydrogen. Expedriments were performed on a standard pulsed NMR spectrometer using standard cryogenic techniques to achieve low temperatures [7].

## 3. Results

Figure 1 shows the low temperature (8 K) NMR lineshapes for three samples of a-Si:H made by the HWCVD technique and one sample made by the PECVD technique. In the PECVD sample the two peaks near ± 100

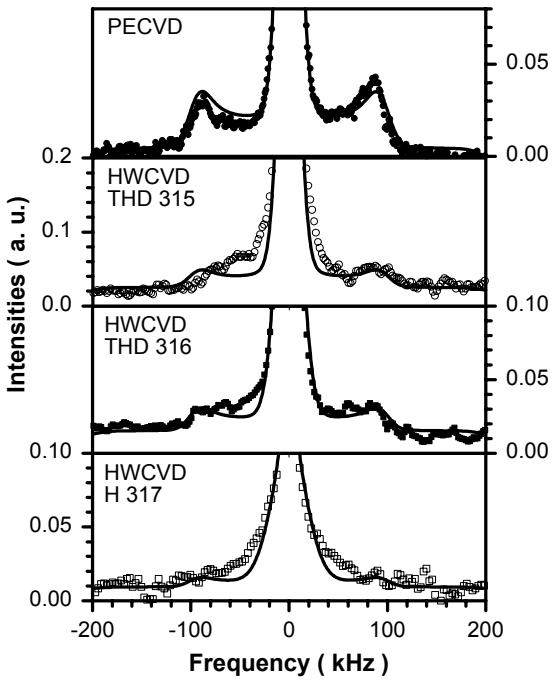


Fig. 1 NMR lineshape at 8 K in three samples of a-Si:H as described in the text.

kHz are due to ortho-$H_2$ molecules that are "frozen" into the ground rotational state (Pake doublet). The central region of the spectrum contains the two $^1$H NMR signals due to bonded hydrogen in the dilute and clustered environments.

Note that in the three HWCVD samples the two Pake-doublet peaks due to molecular hydrogen are either less pronounced or absent. This narrowing occurs because the molecular hydrogen is tumbling rapidly even at 8 K in the HWCVD samples. Qualitatively, the tumbling rates increase for the bottom three samples in the figure (samples THD315, THD316, and H317). Sample H317 exhibits the fastest tumbling rate at 8 K. Samples THED315 and THD316 were made under similar conditions except that sample THD317 was made with a screen to protect the substrate from a direct view of the hot filament used to decompose the silane. Sample H317 is similar to those samples that have shown the lowest internal friction [8].

Figure 2 shows a direct comparison between the PECVD sample and the HWCVD sample (H317) at 8 K. Note the well defined Pake-doublet in the PECVD sample (solid circles) and the "motionally narrowed" molecular hydrogen contribution in the HWCVD sample (open squares.) The dashed line is a fit to the narrowed molecular hydrogen contribution to the NMR in the HWCVD sample. The width of this line is about 70 kHz (full width at half maximum).

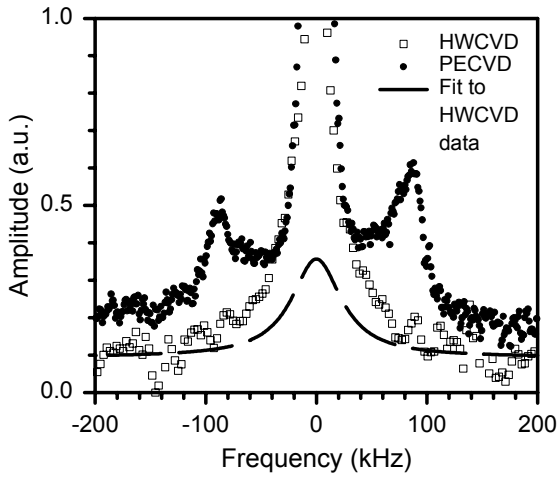


Fig. 2 Comparison of ortho-molecular hydrogen lineshapes in PECVD and HWCVD a-Si:H. See text for details.

## 4. Discussion

For both the PECVD and the HWCVD samples the concentrations of ortho-molecular hydrogen obtained from the direct measurements described above are one order of magnitude greater than those inferred from the spin-lattice relaxation time measurements, which probe the molecular hydrogen indirectly through their effect on the relaxation of the bonded hydrogen. This result establishes an accurate measurement of the concentration of $H_2$ for the first time.

The second important discovery is the much lower freezing temperature for $H_2$ in the HWCVD samples. Because the freezing temperature is controlled by the electric field gradient due to distortions in the silicon lattice, we infer that the HWCVD samples, and the sample with very low internal friction in particular, have a more ordered silicon lattice. This result is consistent with the conclusions drawn from the internal friction measurements [8].

## 5. Summary

The concentration of molecular hydrogen in a-Si:H is found to be about 10% of the total hydrogen concentration incorporated into both PECVD [9] and HWCVD samples. There are two types of sites for the molecular hydrxogen, one which is effective in relaxing the H NMR due to bonded hydrogen and one which is not. Comparison of the lineshapes at 8 K between the PECVD and HWCDVD samples suggests that the HWCVD samples have a more ordered silicon matrix.

## 6. Acknowledgements

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